

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

WARTIME REPORT

ORIGINALLY ISSUED

March 1945 as
Advance Restricted Report E5B14

ULTRAVIOLET SPECTROCHEMICAL ANALYSIS FOR
AROMATICS IN AIRCRAFT FUELS

By Alden P. Cleaves

Aircraft Engine Research Laboratory
Cleveland, Ohio

PROPERTY OF JET PROPULSION LABORATORY LIBRARY
CALIFORNIA INSTITUTE OF TECHNOLOGY



WASHINGTON

NACA WARTIME REPORTS are reprints of papers originally issued to provide rapid distribution of advance research results to an authorized group requiring them for the war effort. They were previously held under a security status but are now unclassified. Some of these reports were not technically edited. All have been reproduced without change in order to expedite general distribution.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

ADVANCE RESTRICTED REPORT

ULTRAVIOLET SPECTROCHEMICAL ANALYSIS FOR

AROMATICS IN AIRCRAFT FUELS

By Alden P. Cleaves

SUMMARY

Object. - The object of the tests was to verify and extend ultraviolet spectroscopic techniques for applications to the analysis of aviation fuels for their aromatic constituents.

Scope. - The suitability and accuracy of a photographic technique and of a spectrophotometric technique for simultaneous qualitative and quantitative analysis were investigated. Extinctions at maxima and minima of absorption in spectrograms of nine aromatics photographed with a grating spectrograph were measured on a photoelectric densitometer. The reproducibility and accuracy of this technique were ascertained. Data for plotting the absorption spectra of eight aromatics were obtained with a quartz photoelectric spectrophotometer, and a method suitable for analyzing aviation gasoline for benzene and toluene was applied to four fuels. A similar analysis technique was established for binary mixtures of the aromatics 1,3,5-trimethylbenzene and propylbenzene. The results of the analyses were checked for olefinic interference. Spectrophotometric extinctions of mixtures of m-xylene and p-xylene were correlated with composition as an example of testing relative purity. Measurements on binary mixtures of aromatics were exploratory and problems connected with distillation and analysis of more complex mixtures of aromatics that are probable in the boiling range above about 125° C have not yet been investigated.

Summary of results. - Spectrophotometric analysis, which was found to be both more accurate and more rapid than the spectrographic technique, was used to determine aromatic concentrations in two types of binary mixture with a root-mean-square error of 1 to 3 percent of the total present, for the range of concentrations investigated.

A sample of 65-octane-number gasoline was found to contain 1.1 percent of benzene and 1.8 percent of toluene; because only these two aromatics were present, distillation was unnecessary for the analysis. The spectrophotometric method supplemented by distillation gave the following results for three other fuels:

Fuel	Benzene (percent by volume)	Toluene (percent by volume)
AN-F-28	1.4	4.0
AN-F-29 (140-P)	1.3	5.6
M-4 reference fuel	.5	1.4

Conclusions. - These tests indicate that simple, rapid, and accurate analysis of binary mixtures of aromatics is feasible with an ultraviolet photoelectric spectrophotometer. This instrument is preferable in all three of these characteristics to a spectrograph-and-densitometer combination. The spectrophotometric-analysis technique could probably be extended to more complex mixtures. If this technique were supplemented by suitable fractional distillation, it would be comprehensive for nearly all the aromatics in aviation fuels.

INTRODUCTION

Many of the aromatic hydrocarbons that boil in the gasoline range (20° C to 180° C) have high engine-performance ratings and may therefore be desirable constituents of fuels for military aircraft. Selective control of producing and blending of the aromatic components to secure best fuel blends requires simple, rapid, and reliable methods of analysis for the individual aromatics. Quantitative analysis for aromatics is also valuable in connection with a program for testing the engine performance of current aviation fuels. Because of recent improvements in the quantitative response of photoelectric receivers, their application in commercially available spectrophotometers, such as the quartz photoelectric spectrophotometer described in reference 1, now makes possible the widespread adoption of an improved aromatic-analysis technique based on the intense absorption by aromatics in the region of the ultraviolet spectrum from 2300 A to 2800 A.

The few chemical methods of quantitative analysis for specific aromatics that have proved adequate for mixtures as complex as typical aircraft fuels are usually slow and difficult. Isolation of the individual aromatics in narrow cuts by distillation of the fuels and

subsequent quantitative determinations by recovery of the aromatics in the cuts from suitable adsorbing materials as described in references 2 and 3 or by other methods such as the freezing-point technique of reference 4 are also difficult and tedious. An accuracy of about 1 percent of the total aromatics was attained by the National Bureau of Standards in such analyses reported in reference 5. For quick estimation of the total aromatics present in a fuel (without distillation) the method of reference 2 may be used.

Information received by the author through the British Central Scientific Office, Washington, D. C. concerning investigations directed by the Spectrographic Subcommittee of the British Technical Advisory Committee reveals that a spectrographic method of detection and estimation of aromatics in mixtures of as many as four components was developed and applied in England before 1943. Spectra of 32 purified aromatics were photographed. In quantitative analysis for the four aromatic C_8 isomers, based on visual matching of image densities in the photographed absorption spectra, an accuracy of approximately 3 percent of the total amount present was attained.

Information describing a spectrophotometric method of quantitative analysis for benzene, toluene, and four aromatic C_8 isomers in aircraft fuels was obtained from Esso Laboratories. In this method, procedure and computations for the analyses were so systematized that analysis of a sample could be completed by a relatively inexperienced operator with a probable error of 1 or 2 percent.

Experimental investigations were conducted at the NACA Cleveland laboratory during the summer of 1943 to test the experimental technique used for the investigations directed by the British Spectrographic Subcommittee, which was improved in the tests reported herein by measuring image densities with a photoelectric densitometer, and to verify, apply, and extend the spectrophotometric technique described by Esso Laboratories. Measurements on binary mixtures of aromatics were exploratory, and problems connected with distillation and analysis of more complex mixtures of aromatics that are probable in the boiling range above about $125^{\circ}C$ have not yet been investigated. Certain general principles discussed in the first part of the report are followed by a description and a discussion of the experimental results.

LIST OF SYMBOLS

- c concentration of aromatics in solution, grams per liter
- d thickness of liquid in the absorption cell, centimeters

- E extinction ($E = \log I_0/I$)
- I intensity transmitted through solution in a cell
- I_0 intensity transmitted through solvent in a cell
- k specific extinction at each wavelength defined as the extinction due to concentration of 1 gram per liter of a pure component in a cell 1 centimeter thick
- λ wavelength, Angstroms
- T transmission, percent ($T = 100 I/I_0$)

Numerical subscripts attached to c designate respective components of a mixture; attached to E they designate a selected wavelength. Letter subscripts attached to E designate components. The double numerical subscripts attached to k designate component and wavelength, respectively.

PRINCIPLES OF ABSORPTION ANALYSIS AND DESCRIPTION OF THE METHOD

The Problem of Spectroscopic Interference

When two or more compounds in a multicomponent mixture produce appreciable absorption at a given wavelength, their absorption is said to interfere. In order to perform a successful analysis in such a case, a scheme must be devised that in its application isolates the absorption due to each interfering component and evaluates the concentration of each component.

In the ultraviolet region between 2200 Å and 2800 Å, aromatic compounds absorb strongly; whereas paraffins, naphthenes, and olefins do not. The absence of interference due to paraffins, naphthenes, and olefins in gasoline makes this region of the ultraviolet spectrum particularly suitable for the aromatic analysis of fuels. Diolefins, conjugated diolefins, and styrenes, which do have some absorption at wavelengths less than 2500 Å, are usually minor components of fuels if they are present at all. They are sufficiently reactive that mild reagents may be used to reduce their concentrations to small values whenever their interference is detected. A brief spectrometric check procedure for detecting olefinic interference is described in a subsequent section The Check Procedure and an explanation of a particular case is presented in appendix A.

The spectrograms in figure 1 show the general character of aromatic absorption arranged to emphasize differences that have been observed. The bands (dark regions in the spectra of fig. 1) of the longest wavelengths in the aromatic spectra will hereinafter be called "first bands." Shifts in the wavelengths of these first bands are particularly noteworthy. Consideration of the wavelengths of first bands suggests that the spectra of aromatics be arranged in three groups according to the following tabulation:

Group	Spectrogram	Number of substitutions in the aromatic ring	Wavelength region where first bands occur, A
I	8	0	2600 to 2610
II	5, 6, 7	1	2650 to 2690
III	1, 2, 3, 4	2 and 3	2690 to 2750

British spectrographic research indicates that this grouping is generally valid for molecules having a single ring. One further generalization of considerable usefulness applies to molecules in group III: Two substitutions in the para positions on the ring give rise to spectra that are about twice as intense as other spectra and are characterized by first bands in the vicinity of 2740 A.

Many of the aromatic compounds have approximately six bands arranged in similar patterns. The problem of mutual interference between them becomes more serious as the number of aromatics present in appreciable quantities increases. This fact, however, may not eliminate the usefulness of the ultraviolet method if it can be supplemented by distillation of the fuel in an efficient column into numerous cuts that are subsequently poured together, according to spectroscopic evidence, to form definite fractions. Table I, compiled from data from reference 6 and the Fuel Synthesis Section of the Cleveland laboratory, lists aromatics that boil in the gasoline range in the order of their increasing boiling points. From these data it appears possible to combine the cuts into fractions containing from one to five aromatics according to the following tabulation:

Fraction	Range of boiling points of aromatics in the fraction, °C	Number of aromatics having boiling points in the range
1	20. to 120	2
2	120 to 146	4
3	146 to 155	1
4	155 to 166	3
5	166 to 174	5
6	174 to 180	5

The distillation part of the problem, however, may be so difficult that, for the boiling range from 140° C to 180° C, methods and apparatus similar to those employed by the authors of reference 5 may be necessary; spectrochemical methods may expedite the analysis.

Method of Qualitative and Quantitative Analysis

The first requisite for setting up a method of analyzing a multicomponent mixture is to have a quantitative graph of the absorption spectrum for a pure sample of each component. It is convenient to have these graphs show the variation of specific extinction with wavelength. These absorption curves are then compared and for each component the wavelength of the peak of one of its most intense bands that is not interfered with seriously is selected to characterize that component. The ratios of the specific extinction of the component at its characteristic wavelength to the specific extinctions of the other components at that wavelength should be as large as possible. One extra wavelength, preferably in the vicinity of 2350 Å, may be selected for the purpose of checking the analysis and detecting interference by nonaromatic absorbers.

The absorption of light of a definite wavelength is a function of the number and the character of the molecules in the path of light. According to the Beer-Lambert law:

$$I = I_0 10^{-kcd} \quad (1)$$

$$\log I_0/I = kcd \quad (2)$$

$$kcd = E \quad (3)$$

The product cd is proportional to the number of molecules of a component and the specific extinction k is characteristic of the molecules. Specific extinctions for each pure component at the selected wavelengths may be tabulated as follows:

Wavelength → Component ↓	1	2	3	4	5
1	$k_{1,1}$	$k_{1,2}$	$k_{1,3}$	$k_{1,4}$	$k_{1,5}$
2	$k_{2,1}$	$k_{2,2}$	$k_{2,3}$	$k_{2,4}$	$k_{2,5}$
3	$k_{3,1}$	$k_{3,2}$	$k_{3,3}$	$k_{3,4}$	$k_{3,5}$
4	$k_{4,1}$	$k_{4,2}$	$k_{4,3}$	$k_{4,4}$	$k_{4,5}$

For monochromatic radiation at each of the several selected wavelengths, the extinction of a properly diluted fraction of the fuel in a cell of thickness d is assumed to be equal to the sum of the extinctions of the components multiplied by the cell thickness. Four components require four equations, as follows:

$$E_1 = (k_{1,1}c_1 + k_{2,1}c_2 + k_{3,1}c_3 + k_{4,1}c_4) d \quad (4)$$

$$E_2 = (k_{1,2}c_1 + k_{2,2}c_2 + k_{3,2}c_3 + k_{4,2}c_4) d \quad (5)$$

$$E_3 = (k_{1,3}c_1 + k_{2,3}c_2 + k_{3,3}c_3 + k_{4,3}c_4) d \quad (6)$$

$$E_4 = (k_{1,4}c_1 + k_{2,4}c_2 + k_{3,4}c_3 + k_{4,4}c_4) d \quad (7)$$

Equations (4), (5), (6), and (7) may be solved for the concentrations by familiar methods.

The Check Procedure

An equation for the extinction of the mixture at some wavelength in the interval from 2300 Å to 2400 Å can be used to check for gross inaccuracies in the analysis and to detect interference of nonaromatic components. The check is made by substitution of the values of c in the following equation

$$E_5 = (k_{1,5}c_1 + k_{2,5}c_2 + k_{3,5}c_3 + k_{4,5}c_4) d \quad (8)$$

The presence of interfering absorption only in the interval from 2300 Å to 2400 Å will cause the computed value E_5 to be less than the measured value. From what is known about olefinic absorption, a limit can be assigned to the difference between the two values of E_5 in order that the resulting errors will be properly restricted. This value is herein considered to be 3 percent. Discussion of an application of the check procedure to a particular case of olefinic interference will be found in appendix A. Analysis for aromatics of mixtures containing known amounts of olefins has not been tried at this laboratory, but unpublished information from the Esso Laboratories states that the accuracy of analysis is unaffected when about 10 percent of olefin is present.

Accuracy of Absorption Analysis

The reliability of results obtained by the ultraviolet absorption analysis depends on the purity of the compounds used to determine

the specific extinctions as well as on the validity of Beer's law. The aromatics used in the present tests were carefully prepared by the Fuel Synthesis Section of the Cleveland laboratory under the direction of Dr. L. C. Gibbons and their purity was checked by the most useful properties mentioned in the first paragraph of appendix B. Their indices of refraction given in the seventh column of table I may be compared with the corresponding values in the fifth column taken from Doss (reference 6) as an indication of the purity of the samples used.

Variations of k with concentration, with type of solvent, or with type of solute in a mixture would be evidences of the failure of Beer's law. The constancy of k was verified for the applications in this report.

The authors of reference 7 have developed a complex modification of the foregoing method that permits successful spectrophotometric analysis when the k 's are not constant.

The following brief discussion of one aspect of the expected average spectrophotometer error is included to provide a clearer understanding of the precision possible in this method of analysis. Percentage transmission T is defined as

$$T = 100 I/I_0 \quad (9)$$

Extinction is a function of percentage transmission according to the equation

$$E = \log \frac{100}{T} \quad (10)$$

The instrumental error in the measurement of T is approximately constant. The following tabulation shows the variation of the errors in E that corresponds to an assumed constant error of 0.25 percent in T :

Percentage transmission	Percentage absorption	Extinction	Approximate error in extinction	Approximate percentage error in extinction
90	10	0.05	0.0011	2.2
80	20	.10	.0013	1.3
50	50	.30	.0021	.6
20	80	.70	.005	.8
10	90	1.0	.011	1.1
5	95	1.3	.023	1.8

The values of percentage error in extinction shown in this table emphasize the desirability of choosing a dilution factor or cell thickness that will cause the measured extinctions to lie in the range from 0.3 to 0.6. When an analysis is based on extinctions not in this range, errors larger than the minimum are to be expected.

APPARATUS AND TESTS

Grating Spectrograph and Accessories

A concave grating spectrograph was used for the photographic investigations. The 1.5-meter grating was ruled with 48,000 lines, 1 inch in length, spaced 24,000 lines to the inch. Spectra were photographed in the region from 2200 Å to 4350 Å on a 15-inch length of Eastman Kodak Spectrum Analysis No. 1 Safety film, which is 35 millimeters wide. The dispersion was 7 Å per millimeter. A slit width of 0.06 millimeter was used. A hydrogen-discharge lamp operated on a well-regulated supply of 70 volts direct current was the source of ultraviolet light. Hydrocarbon solutions were contained in a quartz absorption cell of 1-centimeter thickness mounted between the lamp and the slit. A single switch that operated both an electromagnetic shutter and an electric interval timer was used to control the exposure time, which varied from 10 to 320 seconds.

Numerous factors, such as concentration, degree of agitation, temperature, time of immersion in the developer, validity of the reciprocity law, edge effects, stray light, and nonuniformity of film emulsion, are known to affect quantitative comparison of light intensities based on the photometry of photographic images. A uniform procedure was adopted for the purpose of reducing the effect of such factors on accuracy. The concentrations of Kodak Developer D-19, an acid short-stop bath, and Kodak Fixing Bath F-5 were carefully controlled. The films were processed in trays of the solutions that were mechanically rocked in a water bath maintained at 20° C by a thermostat.

Measurements of transmission and wavelengths of images on the films were made with an Applied Research Laboratories - Dietert Comparator Densitometer. On each film three of the eight spectra were photographed through the solvent, whereas the other five exposures were taken through the solution for intervals 2, 4, 8, 16, and 32 times the exposure time through the solvent. The image densities of small adjacent areas on the film were compared only where they nearly matched; consequently, only small intervals on the gamma curves were used. Sliding logarithmic scales were used on the

gamma curve for the wavelength interval considered to convert relative image densities into intensity ratios I_0/I of the light transmitted by the cells. Extinction values could then be calculated from the intensity ratios.

In photographs of the spectra of nine purified aromatics the extinctions at maxima and minima of absorption were determined and tabulated. The suitability and reliability of the spectrographic technique for routine application to quantitative analysis were also briefly investigated.

Quartz Spectrophotometer

The ultraviolet spectrophotometric measurements were made with a commercial quartz spectrophotometer, described in detail in reference 1, which is suitable for measurements in the range from 2200 Å to 10,000 Å. The ultraviolet source was identical with the one used with the grating spectrograph. Two matched 0.5-centimeter quartz cells, one for the solvent and one for the solution, were placed alternately in the monochromatic ultraviolet beam between the exit slit and the photoelectric cell, which was so connected that variation of the voltage was proportional to the intensity of light incident upon the cell. In routine operation a potentiometer in the spectrophotometer was used to take the quotient of the voltages characteristic of the light intensity through the solvent and through the solution. The scale that rotated with the potentiometer knob was uniformly graduated to indicate the value of the quotient, which was percentage transmission, and logarithmically graduated to indicate directly the extinction values for the solution.

A concentration of about 0.04 percent by volume of aromatics in 2,2,4-trimethylpentane obtained from Rohm and Haas Company (less than 0.001 percent of aromatics) was found to be suitable in most cases. This dilution by a factor of 2500 was obtained by double dilution in order to conserve the solvent.

The spectrophotometer was used to obtain data for plotting the absorption spectra of eight aromatics. A method of analysis for benzene and toluene was tested for accuracy and applied to four fuels, and a similar technique for analyzing binary mixtures of 1,3,5-trimethylbenzene and propylbenzene was tested. Spectrophotometric extinctions of mixtures containing m-xylene and p-xylene were correlated with composition as an example of testing relative purity.

RESULTS AND DISCUSSION

Photographic Absorption Spectra

Successive maxima and minima of specific extinctions and corresponding wavelengths accurate to ± 2 Å for the photographed spectra of aromatics 1, 2, 3, 7, 8, 11, 13, 17, and 18 in table I are presented in table II. A positive enlargement of spectrograms of eight aromatics is reproduced in figure 1. Dark regions, as at 2545 Å in spectrogram 8, represent absorption bands. The variation of the sensitivity of the film in this region is shown in spectrogram 9 taken through the solvent, the exposure time being one eighth that for the other spectra. The aromatic 1-methyl-4-isopropylbenzene (spectrogram 4) has such low absorption between 2600 Å and 2400 Å that its spectrum is a fair indication of the film response in this region for an exposure of 200 seconds. Much of the contrast and detail of the original negative is, however, not evident in the reproduced enlargement.

The values in table II are useful for qualitative comparisons and as indications of the relative values of maxima of extinction in the spectra of liquid aromatics when spectroscopic resolution is good. The relatively narrow slit width used (0.05 to 0.1 mm) gave assurance that the breadth and overlapping of the absorption bands as they appeared on the negatives and in figure 1 was characteristic of the liquids and was not due to the limited resolving power of the spectrograph.

Early tests for accuracy and reproducibility of extinction values and investigations of the uniformity of purified aromatic samples by the photographic method indicated that the average error, which was found to be approximately 5 percent, would probably be more than 2 percent at all times unless elaborate precautions were adopted to minimize it. This photographic method involved several separate operations that were time-consuming and the accuracy attained was not adequate for our requirements. Because spectrophotometric measurements could be made faster and with better precision than photographic measurements, the results of the photographic technique were not prepared for routine use in quantitative analysis.

Spectrophotometric Absorption Spectra

The absorption spectra of the pure aromatic hydrocarbons 1, 2, 3, 4, 6, 7, 8, and 11 in table I determined with the quartz spectrophotometer are plotted in figures 2 to 9. Because the method was rapid and accurate, numerous points were measured; hence the form of the curves has significance and is not dependent on fairing.

Individual bands are less well resolved than in the photographic spectra of figure 1 owing to lower dispersion and the use of 0.5-millimeter slit widths on the spectrophotometer. Because tests showed that Beer's law was valid for these slit widths for several bands, these slit widths were adopted as satisfactory when response of the instrument and other factors were considered. The experimental error in setting the wavelength drum on a sharp band was ± 1.0 A, as read on the wavelength scale.

Spectrophotometric Analyses

Binary mixtures. - The specific extinctions for a concentration of 1 gram per liter in a 1-centimeter cell, the working equations, and the results of calculations of the composition of several binary mixtures are given for benzene and toluene in table III and for 1,3,5-trimethylbenzene (mesitylene) and propylbenzene in table IV. The values of some of the specific extinctions are functions of the effective slit width of the spectrophotometer; they may also be affected by other specific characteristics of a particular instrument such as the stray radiation that emerges through the exit slit. None of the specific extinctions reported herein should be adopted for analyses using other spectrophotometers unless comprehensive comparative measurements satisfactorily verify the values. For example, from unpublished data from the American Petroleum Institute Hydrocarbon Research Project obtained with a photoelectric spectrophotometer similar to the one used in the analyses presented herein, the principal band of *p*-xylene reported at 2747 A was computed to have a specific extinction of 4.63, whereas for the same slit widths the value from figure 10 of the present report is 4.95 for the same band located at 2744 A. For a band of *o*-xylene, however, the agreement is better. For the band located at 2710 A on both instruments the specific extinction from the unpublished A.P.I. data is 1.89 and the value from figure 6 of this report is 1.86.

A sample calculation for mixture A of table IV will clarify the method. For that mixture, $E_1 = 0.2750$, $E_2 = 0.3700$, and $E_3 = 0.2810$. Substitution in equations (4) and (5) of specific extinctions from table IV and solution for c_1d and c_2d gives

$$c_1d = 0.7398 E_1 - 0.1051 E_2 \quad (11)$$

$$c_2d = -0.5749 E_1 + 0.6531 E_2 \quad (12)$$

The check equation is

$$E_3 = (0.9660 c_1 + 1.454 c_2) d \quad (13)$$

Substitutions in these equations give

$$c_1d = 0.7398 \times 0.2750 - 0.1051 \times 0.3700 = 0.1645 \quad (14)$$

$$c_2d = -0.5749 \times 0.2750 + 0.6531 \times 0.3700 = 0.0835 \quad (15)$$

$$E_3 = 0.9660 \times 0.1645 + 1.454 \times 0.0835 = 0.2803 \quad (16)$$

Because the values are given for a cell thickness of 1 centimeter, the concentration of 1,3,5-trimethylbenzene c_1 is 0.1645 gram per liter and the concentration of propylbenzene c_2 is 0.0835 gram per liter. In the calculations as well as in columns 1 through 4 of tables III and IV a figure of doubtful significance in the fourth decimal place has been retained as a precaution to prevent introduction of errors that might be caused by its omission.

The result of substituting values in equation (16) indicates that the interference at a wavelength of 2541 Å is

$$\frac{0.2810 - 0.2803}{0.28} = 0.25 \text{ percent, which is less than 3 percent, the}$$

arbitrary maximum that is tolerable according to the discussion in appendix A. The spectrophotometric weight percentages that are tabulated in tables III and IV were computed by dividing the concentrations determined spectrophotometrically by the sum of the concentrations determined by weighing. Because weighing is the more precise method of measurement, weighed values were assumed to be absolutely accurate for the purpose of ascertaining errors. Values in columns 10 and 11, as well as the amounts by which values in column 9 differ from 100 percent, indicate the errors in the analysis.

The magnitudes of the percentage differences in columns 10 and 11 of tables III and IV were used to calculate the root-mean-square error. For the mixtures of benzene and toluene the root-mean-square errors were 1.0 and 1.2 percent, respectively; for 1,3,5-trimethylbenzene and propylbenzene, 2.2 and 0.9 percent, respectively. These errors indicate that the method of analysis is capable of accuracy approximating these percentages of the total aromatics present. The spectrophotometric measurements were made on solutions in which the actual aromatic concentration was the optimum, that is, about 0.04 percent by volume. Because the stated accuracy holds for concentrations as small as this magnitude, spectrochemical detection of aromatics is extremely sensitive. It should be pointed out that errors reported herein are based on total aromatics present; therefore, if a fuel contains 10 percent of aromatics, a reported error of 2 percent would correspond to only 0.2 percent of the total fuel.

A graphical method of determining the composition of binary mixtures is presented in figure 10. A discussion of the application of this method to the problem of testing the purity of aromatics is given in appendix B.

Gasolines. - Results of applying the benzene-toluene analysis to 65-octane-number gasoline and to cuts of three fuels are presented in table V. The first three analyses were made to test the reproducibility of the method in practice. The entire procedure was repeated beginning with the original gasoline sample each time. The maximum deviation from the mean value of the three determinations, whether of benzene, toluene, or of total aromatic content, was less than 1 percent of the amount present. The results are significant to hundredths of percent of the gasoline.

Analyses 4, 5, and 6 reported in table V were made to determine the effect of variation of concentration in the cell by a factor of 5 and also to check the validity of Beer's law. The cut of AN-F-28 fuel used in these analyses was the only cut obtained with a very simple still. The presence of considerable toluene in the 70° C to 100° C fraction is evidence of the poor cutting. In this test the extinction readings on the spectrophotometer fell in the optimum range from 0.3 to 0.6 only for a dilution factor of 250. In spite of this source of slightly increased errors, the comparative accuracy of the three analyses was as good as that attained in the first three reported. The numerical results of these analyses should not be taken as indications of the true composition of the gasoline but should be compared as evidence of reproducibility of the analysis.

Analyses 7 to 12 in table V are independent applications of the method to gasoline cuts obtained in a still of 40 theoretical plates. The results are reliable indications of the aromatic content of the specified fractions.

CONCLUSIONS

Spectrophotometric analyses of synthetic binary mixtures of benzene and toluene and of 1,3,5-trimethylbenzene and propylbenzene together with analyses of fuel cuts containing only benzene and toluene indicate that simple, rapid, accurate analysis of binary mixtures of aromatics is feasible with an ultraviolet photoelectric spectrophotometer. This instrument is preferable in all three of these characteristics to a spectrograph-and-densitometer combination.

The spectrophotometric-analysis technique could probably be extended to more complex mixtures. If this technique were supplemented by suitable fractional distillation, it would be comprehensive for nearly all aromatics in aviation fuels.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio.

APPENDIX A

SIGNIFICANCE OF THE CHECK PROCEDURE

Application to numerical accuracy. - The following discussion of the effects of errors owing to any causes in the values of E_1 , E_2 , and E_3 for the case of 1,3,5-trimethylbenzene and propylbenzene is applicable to other binary mixtures. The equations for the concentrations, when the cell thickness d is 1 centimeter, are

$$c_1 = 0.7398 E_1 - 0.1050 E_2 \quad (11)$$

$$c_2 = -0.5749 E_1 + 0.6531 E_2 \quad (12)$$

and the check equation is

$$E_3 = 0.9660 c_1 + 1.454 c_2 \quad (13)$$

A positive error ΔE_1 in E_1 because of interference or other causes tends to increase c_1 and to decrease c_2 . If c_2 is very small, such an error might possibly lead to negative values of concentration. A positive error in E_2 would evidently have an opposite effect on the concentrations. Tolerance of a 3-percent variation between the computed and the measured value of E_3 would generally permit errors of 3 percent in E_1 and E_2 to remain undetected, especially if the errors were both positive or both negative. Errors larger than about 5 percent would often be detected.

Application to detection of olefins. - The check procedure is of particular value for the detection of interference owing to olefinic absorption, which is small at 2600 A but which increases constantly as values of wavelength decrease. An example using approximate specific extinctions of the olefin 2,4,4-trimethyl-1-pentene measured at this laboratory will reveal the advantages of a wavelength in the interval from 2300 A to 2400 A.

The following tabulation shows the extinctions and the relative extinctions characteristic of 10 grams per liter of 2,4,4-trimethyl-1-pentene, 0.5 gram per liter of 1,3,5-trimethylbenzene, and 0.5 gram per liter of propylbenzene each in a 1-centimeter cell:

Wave-length, λ (A)	2,4,4-Tri- methyl-1- pentene, E_A	1,3,5-Tri- methyl- benzene, E_B	Extinc- tion ratio, E_A/E_B (percent)	Propyl- benzene, E_C	Extinc- tion ratio, E_A/E_C (percent)
2350	0.16	0.25	64	0.16	100
2400	.08	.20	40	.24	33
2541	.02	.48	4.2	.73	2.6
2610	.01	.68	1.5	.87	1.2
2719	.007	.77	.9	.12	5.8

In the region used for analysis, the olefinic absorption is about 2 percent of the aromatic absorption. The errors in the computed aromatic concentrations because of the presence of the olefin would be

$$\Delta c_1 = 0.7398 \times 0.007 - 0.1051 \times 0.01 = 0.0042 \text{ gram/liter}$$

$$\Delta c_2 = -0.5749 \times 0.007 + 0.6531 \times 0.01 = 0.0025 \text{ gram/liter}$$

These errors are 0.8 and 0.5 percent, respectively, of the assumed aromatic concentrations. In this case a concentration of olefin 20 times that of the aromatic would be tolerable.

At 2541 A, the wavelength used herein for checking, the olefinic absorption amounts to 4.2 percent of the aromatic absorption in one case and 2.6 percent for the other. The arbitrary limit of 3 percent apparently limits the presence of an olefin to a concentration of 20 times that of the aromatic concentration in the case of 2,4,4-trimethyl-1-pentene. At 2350 A the olefin present at this concentration causes absorption of the same order of magnitude as that of each aromatic. Wavelengths in the suggested interval (2300 A to 2400 A) are evidently better than the longer wavelengths used herein to check for olefinic interference.

APPENDIX B

SPECTROPHOTOMETRIC PURITY TESTING

In connection with ultraviolet spectrophotometric analysis for aromatics, the problem of determining the relative purity of an aromatic hydrocarbon when no absolutely pure sample is available is common. Physical constants of the pure compound, such as boiling point, freezing point, density, and index of refraction, are often useful for this purpose. These properties of some isomers, which may occur in mixtures, are so similar, however, that they are inadequate. Ultraviolet absorption spectra constitute another type of physical data that may be most helpful for some cases.

In order to appraise the usefulness of such data the spectrophotometric extinctions of seven binary mixtures of m-xylene and p-xylene, obtained during purification of p-xylene by crystallization, were measured at three selected wavelengths. The compositions of these mixtures had previously been estimated by referring their freezing points to a freezing point-composition diagram. The data plotted in figure 10 show the extinctions of the mixtures as functions of the estimated composition. The important features of this figure are the linearity of the graphs and the magnitude of the variation of the extinction at each wavelength with composition. As a criterion of composition, the line in figure 10 for the principal peak of p-xylene at 2744 Å appears to be preferable to the freezing-point diagram in the range from 5 to 95 percent. The slope of this line is 0.04 unit of extinction for each 1-percent change of composition. Measurement of extinctions accurate to 0.01 would, therefore, make possible the detection of 0.25-percent variation in composition.

When several unknown impurities are present, the difficulty of spectroscopic determination of purity is considerably increased, but spectrophotometric data are often desirable even in this case. Knowledge of the extinction value at 100 percent, however, is usually dependent upon the availability of a sample that is absolutely pure or of two or more mixtures whose compositions are accurately known.

REFERENCES

1. Carey, H. H., and Beckman, Arnold O.: A Quartz Photoelectric Spectrophotometer. Jour. Optical Soc. Am., vol. 31, no. 11, Nov. 1941, pp. 682-689.
2. Mair, Beveridge J., and Forziati, Alphonse F.: Analytical Determination of Aromatic Hydrocarbons by Adsorption. Res. Paper 1582, Nat. Bur. Standards Jour. Res., vol. 32, no. 4, April 1944, pp. 151-164.
3. Mair, Beveridge J., and Forziati, Alphonse F.: Separation and Recovery of Aromatic Hydrocarbons from Paraffins and Naphthenes by Adsorption. Res. Paper 1583, Nat. Bur. Standards Jour. Res., vol. 32, no. 4, April 1944, pp. 165-183.
4. Streiff, Anton J., and Rossini, Frederick D.: Methods for Determining Individual Hydrocarbons in Mixtures of Hydrocarbons by Measurement of Freezing Points. Res. Paper 1584, Nat. Bur. Standards Jour. Res., vol. 32, no. 5, May 1944, pp. 185-195.
5. Forziati, Alphonse F., Willingham, Charles B., Mair, Beveridge J., and Rossini, Frederick D.: Hydrocarbons in the Gasoline Fraction of Seven Representative Crudes, Including All the Distillate to 102° C and the Aromatics to 160° C. Res. Paper 1571, Nat. Bur. Standards Jour. Res., vol. 32, no. 1, Jan. 1944, pp. 11-37.
6. Doss, M. P.: Physical Constants of the Principal Hydrocarbons. The Texas Co. (New York), 4th ed., 1943.
7. Brattain, R. Robert, Rasmussen, R. S., and Cravath, A. M.: A Spectrophotometric Method for the Analysis of Multi-Component Mixtures and Its Infra-Red Application. Jour. Appl. Phys., vol. 14, no. 8, Aug. 1943, pp. 418-428.

TABLE I - PHYSICAL PROPERTIES OF AROMATIC HYDROCARBONS

[Boiling point, 80° C to 180° C; index of refraction at 20° C for sodium light, n^{20}_D ; specific gravity at 20° C relative to water at 4° C taken as unity, d^{20}_4 .]

Distil- lation frac- tion	Hydrocarbon	Boiling point at 760 mm, °C (a)	Freezing point, °C (a)	n^{20}_D (a)	d^{20}_4 (a)	n^{20}_D (b)
1	1 Benzene	80.09	5.51	1.5012	0.87893	1.5003
	2 Toluene	110.65	-95.0	1.49685	.8669	1.4967
2	3 Ethylbenzene	136.15	-94.96	1.49587	0.86690	1.49561
	4 p-Xylene	138.4	13.21	1.4953	.8610	1.4959
	5 m-Xylene	139.2	-47.8	1.4971	.86416	-----
	6 o-Xylene	144.5	-25.0	1.5054	.8801	1.5052
3	7 Isopropylbenzene	152.4	-96.1	1.4912	0.8615	1.49107
4	8 Propylbenzene	159.18	-100.1	1.4919	0.8618	1.4918
	9 1-Methyl-4-ethyl- benzene	162.5	-63.7	1.4952	.8618	-----
	10 1-Methyl-3-ethyl- benzene	161.5 to 162.5	-----	^c 1.498 ^{17.9}	.8690	1.498
	11 1,3,5-Trimethyl- benzene	164.6	-44.7	1.4991	.8653	1.49931
	12 1-Methyl-2-ethyl- benzene	164.8	-68.1	1.5041	.8810	-----
5	13 tert-Butylbenzene	167.0	-58.1	^c 1.4905 ²⁵	^c 0.8623 ²⁵	1.49240
	14 1,2,4-Trimethyl- benzene	169.18	-44.09	1.5048	.8762	-----
	15 1-Methyl-2-tert- butylbenzene	170.0	-----	^c 1.49423 ¹⁷	-----	-----
	16 Isobutylbenzene	170.0	-52	1.493	.8626	-----
	17 sec-Butylbenzene	171.0	-82.7	1.4880	^c .8577 ^{25/25}	1.48988
6	18 1-Methyl-4- isopropylbenzene	175.0	-68.8	1.4933	0.8644	1.49000
	19 1-Methyl-2- isopropylbenzene	175 to 176	-73.5	1.5003	.876	-----
	20 1-Methyl-3-iso- propylbenzene	175.6 to 175.8	-75.0	1.4920	.8606	-----
	21 1,2,3-Trimethyl- benzene	176.1	-25.4	^c 1.5107 ²⁵	.8951	-----
	22 1,2-Diethyl- benzene	176 to 177	<-20.0	^c 1.50257 ²²	^c .8795 ²²	1.50257

^aValues are from reference 6.

^bValues for compounds furnished by the AERL Fuel Synthesis Section.

^cNumerical exponents denote temperatures that differ from the specified standard values.

TABLE II - MAXIMA AND MINIMA IN THE ULTRAVIOLET ABSORPTION SPECTRA OF SEVERAL AROMATICS DETERMINED WITH A 1.5-METER GRATING SPECTROGRAPH AND A PHOTOELECTRIC COMPARATOR DENSITOMETER

Solvent, isooctane; slit width, 0.06 millimeter.
Wavelength λ , A; specific extinction, k.

Benzene	Toluene		Ethylbenzene		Isopropylbenzene		Propylbenzene		1,3,5-Tri-methylbenzene		tert-Butylbenzene		sec-Butylbenzene		1-Methyl-4-isopropylbenzene	
	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k	λ	k
2680	0.11		2686	2.85	2684	2.10	2676	1.70	2683	1.87	2721	1.94	2679	1.65	2730	4.63
2665	.071		2676	1.00	2668	1.16	2663	1.04	2670	1.04	2704	1.22	2665	.97	2711	1.34
2608	2.23		2652	2.03	2645	1.97	2641	1.61	2648	1.67	2679	1.84	2642	1.57	2671	3.57
2590	.34		2640	1.59	2632	1.59	2630	1.22	2637	1.39	2672	1.74	2630	1.12	2661	3.06
2546	3.29		2619	3.29	2612	2.68	2608	2.13	2615	2.23	2606	1.42	2610	2.09	2649	3.89
2523	.63		2611	2.32	2602	2.29	2600	1.85	2606	2.00	2596	1.39	2601	1.84	2622	2.11
2487	2.54		2603	2.65	2593	2.48	2589	2.07	2592	2.14	2575	1.67	2599	2.09	2592	2.57
2470	.60		2577	1.88	2568	1.80	2561	1.40	2570	1.51	2555	1.06	2564	1.40		
2430	1.43		2555	2.21	2551	2.04	2545	1.68	2552	1.77	2525	1.35	2548	1.67		
2415	.49		2549	2.03	2542	1.97	2539	1.64	2544	1.74	2488	.87	2541	1.62		
2380	.66		2540	2.12	2533	2.03	2529	1.70	2534	1.79	2470	.96	2530	1.74		
					2500	1.31	2496	1.14					2500	1.10		
					2480	1.38	2475	1.23					2475	1.22		

National Advisory Committee
for Aeronautics

TABLE III - SPECTROPHOTOMETRIC ANALYSES OF BINARY MIXTURES OF BENZENE AND TOLUENE

Mixture	Concentration in cell (gram/liter)		Spectrophotometric		Weight (percent)		Sum of spectro- photo- metric weights (percent)	Difference between weighed percent- ages and spectro- photometric percentages		E ₃			
	Weighted	Spectrophotometric	Weighted	Spectrophotometric	Ben- zene	Tol- uene	Ben- zene	Tol- uene	Meas- ured	Com- puted			
Hydrocarbon	Specific extinction k												
			λ, 2686 Å	λ, 2546 Å	λ, 2487 Å								
Benzene c ₁	k _{1,1} = 0.1468		k _{1,2} = 2.469		k _{1,3} = 2.003								
Toluene c ₂	k _{2,1} = 2.148		k _{2,2} = 1.953		k _{2,3} = 1.365								
$\begin{bmatrix} c_1 d = -0.3893 E_1 + 0.4281 E_2 \\ c_2 d = 0.4921 E_1 - 0.0293 E_2 \\ E_3 = (2.003 c_1 + 1.365 c_2) d \end{bmatrix}$													
	1	2	3	4	5	6	7	8	9	10	11	12	13
A	0.2028	0.3196	0.1943	0.3195	38.8	61.2	37.2	61.2	98.4	1.6	0	0.808	0.825
B	.4097	.6468	.4141	.6200	38.8	61.2	39.2	58.7	97.9	.4	2.5	1.636	1.676
C	.2679	.1598	.2622	.1640	62.6	37.4	61.3	38.3	99.6	1.3	.9	.750	.748
D	.1014	.3308	.0983	.3307	33.5	76.5	22.7	76.5	99.2	.8	0	.642	.648
E ^a	.2054	.3243	.2091	.3275	38.8	61.2	39.5	61.9	101.3	.7	.6	.850	.866
F ^a	.2054	.3243	.2050	.3196	38.8	61.2	38.7	60.3	99.0	.1	.9	.830	.846

^aSynthetic hydrocarbon mixture containing benzene and toluene in amounts quantitatively equivalent to those found in 65-octane-number aviation gasoline.

TABLE IV - SPECTROPHOTOMETRIC ANALYSES OF BINARY MIXTURES OF
1,3,5-TRIMETHYLBENZENE (MESITYLENE) AND PROPYLBENZENE

Hydrocarbon		Specific extinction k											
		λ, 2719 Å		λ, 2610 Å		λ, 2541 Å							
1,3,5-Trimethylbenzene c ₁		k _{1,1} = 1.545		k _{1,2} = 1.360		k _{1,3} = 0.9650							
Propylbenzene c ₂		k _{2,1} = 0.2487		k _{2,2} = 1.750		k _{2,3} = 1.454							
<div>$c_1 d = 0.7398 E_1 - 0.1051 E_2$ $c_2 d = -0.5749 E_1 + 0.6531 E_2$ $E_3 = (0.9660 c_1 + 1.454 c_2) d$</div>													
Mix- ture	Concentration in cell (gram/liter)		Weight (percent)		Sum of spectro- photo- metric weights (percent)	Difference between weighed percent- ages and spectro- photometric percentages			E ₃				
	Weighed	Spectrophoto- metric	Weighed	Spectrophoto- metric		1,3,5- Tri- methyl- benzene	Propyl- benzene	1,3,5- Tri- methyl- benzene	Meas- ured	Com- puted			
A	0.1684	0.0846	0.1645	0.0835	66.6	33.4	65.0	33.0	98.0	1.6	0.4	0.201	0.280
B	.6770	.3400	.6468	.3408	66.6	33.4	63.6	33.5	97.1	3.0	.1	1.116	1.112
C	.4565	.9193	.4255	.9036	33.2	66.8	30.9	65.7	96.6	2.3	1.1	1.736	1.725
D	.0657	.6794	.0545	.6675	8.8	91.2	7.3	89.6	96.9	1.5	1.6	1.003	1.023
E	.6480	.0682	.6637	.0672	90.5	9.5	92.7	9.4	102.1	2.2	.1	.741	.7388

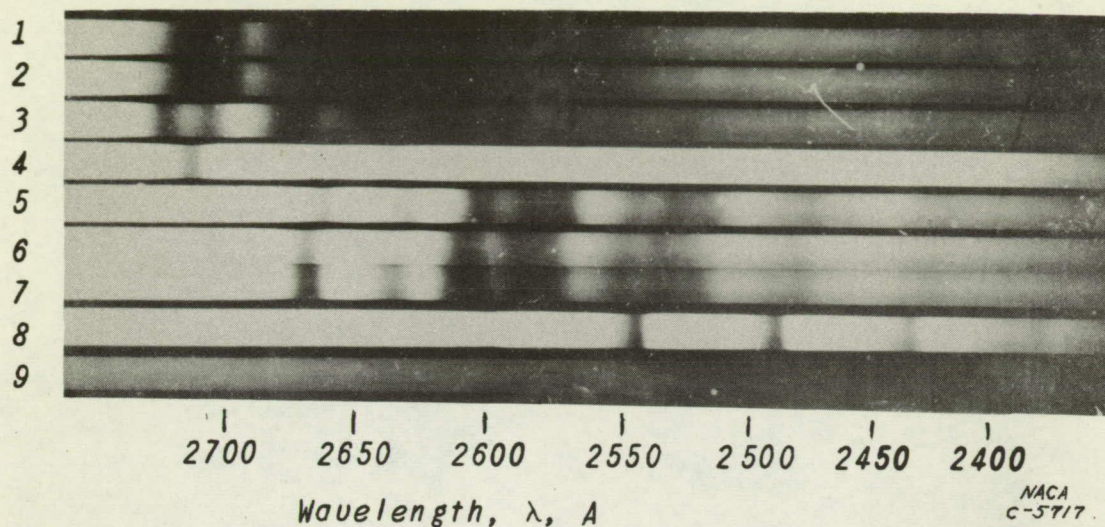
National Advisory Committee for Aeronautics

TABLE V - SPECTROPHOTOMETRIC ANALYSES OF A FUEL AND CUTS OF FUELS FOR BENZENE AND TOLUENE

Analysis	Cut boiling range (°C)	Fuel	Dilution factor	Concentration in cell (gram/liter)		Percentage by volume in fuel		E ₃	
				Benzene	Toluene	Benzene	Toluene	Measured	Computed
1	-----	65 octane number	48	0.2007	0.3298	1.10	1.84	0.850	0.852
2	-----	65 octane number	48	.2002	.3335	1.10	1.86	.844	.856
3	-----	65 octane number	48	.1972	.3282	1.08	1.83	.826	.843
4	70 to 100	AN-F-28	125	.3543	.3639	.772	.804	1.202	1.206
5	70 to 100	AN-F-28	250	.1755	.1826	.764	.808	.602	.601
6	70 to 100	AN-F-28	625	.0708	.0743	.771	.821	.246	.243
7	20 to 95	AN-F-28	125	.205	.016	1.29	.10	.453	.432
8	95 to 125	AN-F-28	625	.0026	.155	.06	3.26	.230	.216
9	50 to 90	AN-F-29 (140-P)	165	.328	.098	1.26	.03	.694	.670
10	90 to 115	AN-F-29 (140-P)	300	.008	.578	.08	5.46	.790	.808
11	90 to 115	AN-F-29 (140-P)	244	.004	.711	.04	5.58	.970	.980
12	24 to 120	M-4 reference fuel	250	.051	.135	.53	1.42	.282	.285

National Advisory Committee
for Aeronautics

Spectrogram



Spectrogram	Substance in cell	Exposure (sec)	Concen- tration in cell (grams/liter)
1	1,3,5-Trimethylbenzene	200	0.69
2	Diethylbenzene mixture	200	.34
3	Xylene mixture	200	.26
4	1-Methyl-4-isopropylbenzene	200	.17
5	Isopropylbenzene	200	.43
6	Propylbenzene	200	.43
7	Ethylbenzene	200	.43
8	Benzene	200	.17
9	Isooctane solvent	25	690

Figure 1. - Positive enlargement of nine spectrograms.
X2. Slit width, 0.10 millimeter; cell thickness,
1.00 centimeter.

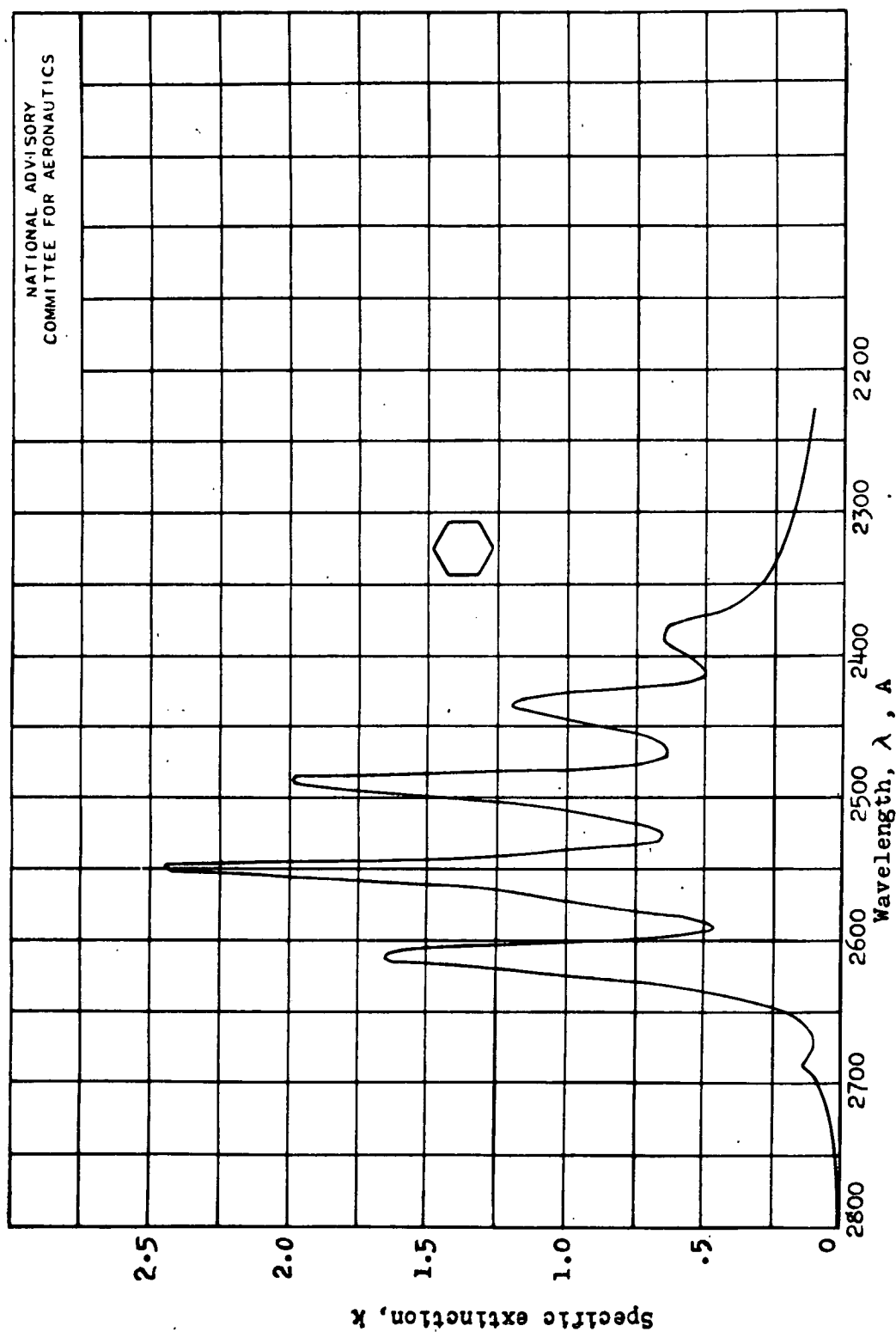


Figure 2. - Ultraviolet absorption spectrum of benzene determined by photoelectric spectrophotometer. Solvent, isooctane; slit widths, 0.50 millimeter.

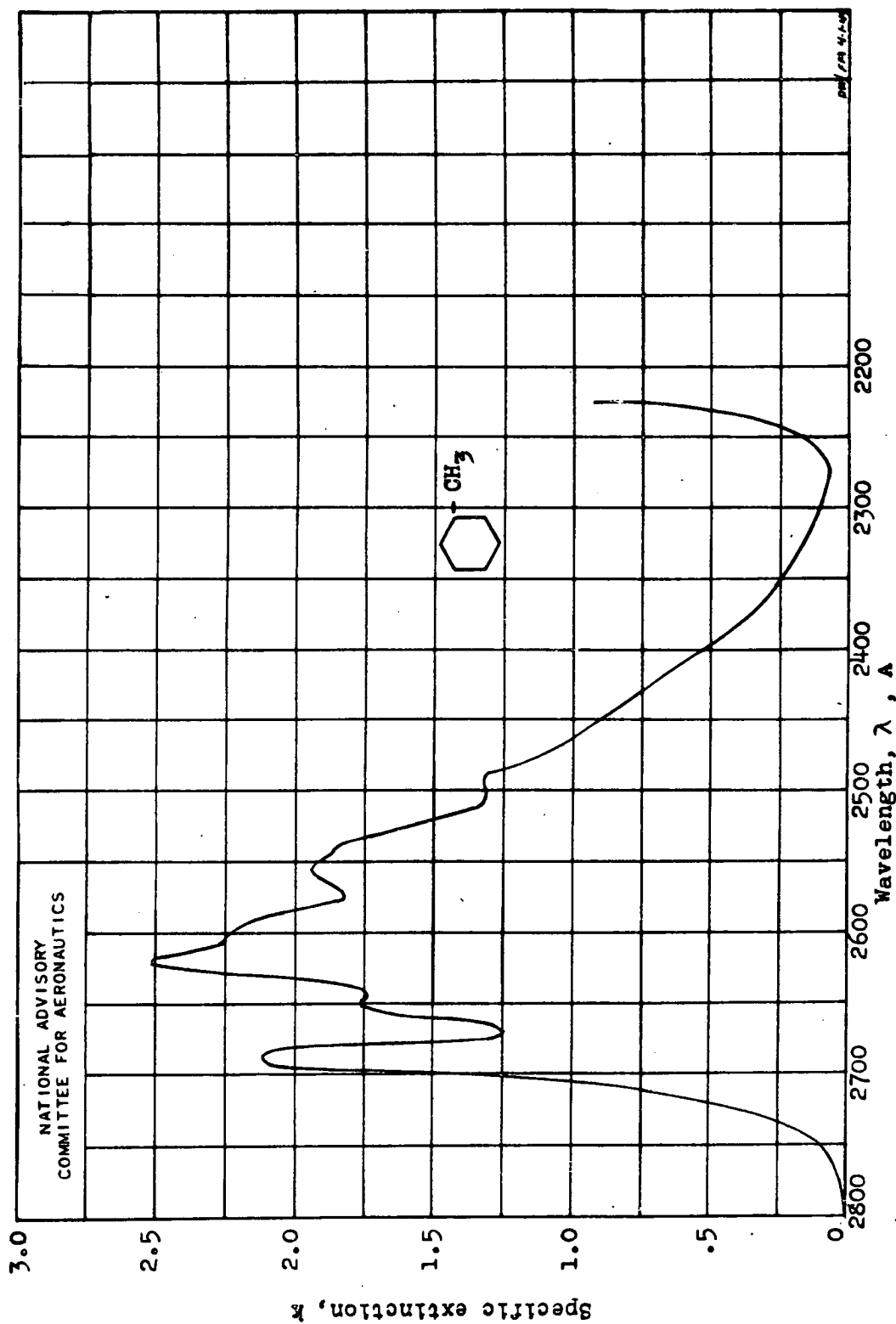


Figure 3. - Ultraviolet absorption spectrum of toluene determined by photoelectric spectrophotometer. Solvent, iso-octane; slit widths, 0.50 millimeter.

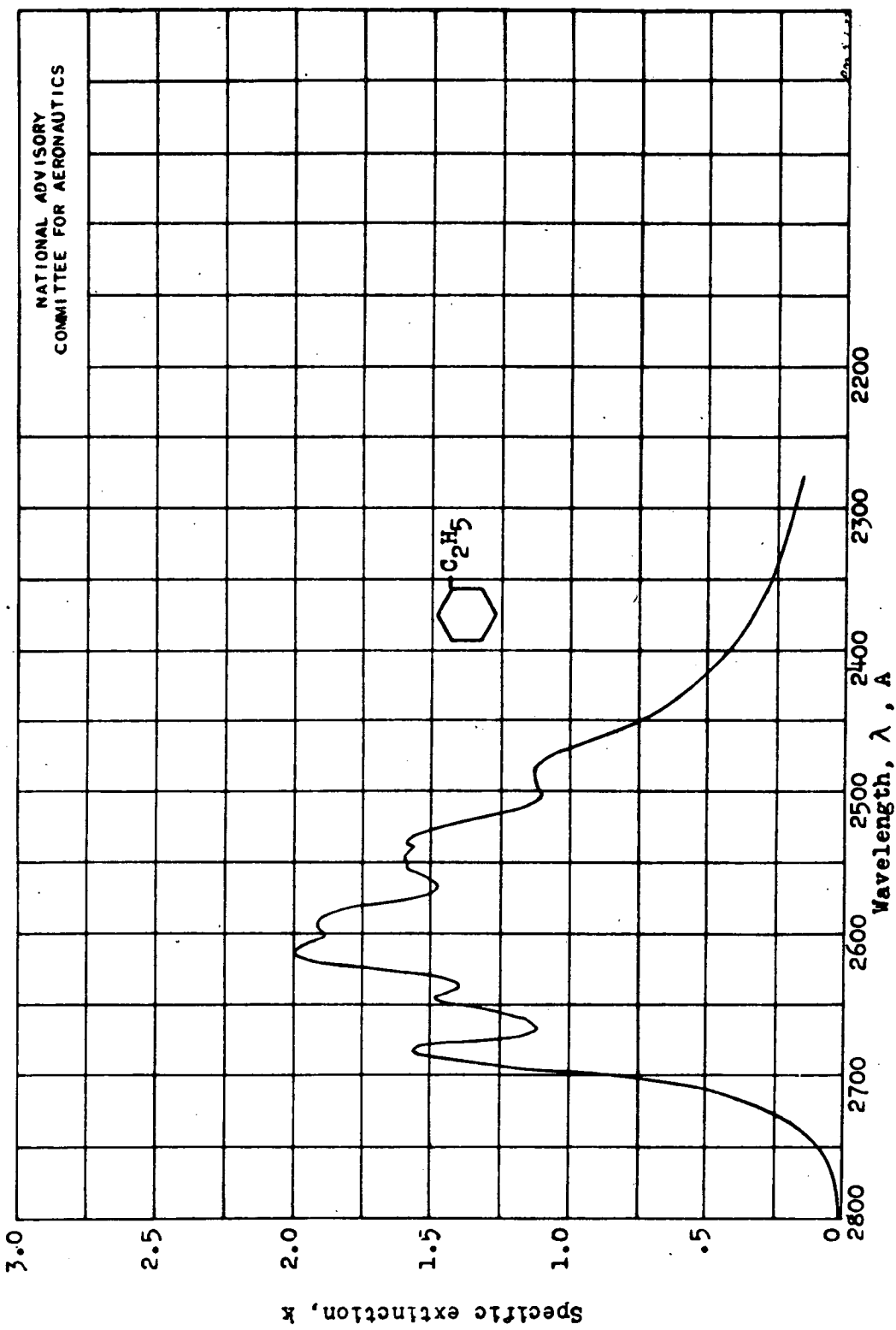


Figure 4. - Ultraviolet absorption spectrum of ethylbenzene determined by photoelectric spectrophotometer. Solvent, isooctane; slit widths, 0.50 millimeter.

NATIONAL ADVISORY
COMMITTEE FOR AERONAUTICS

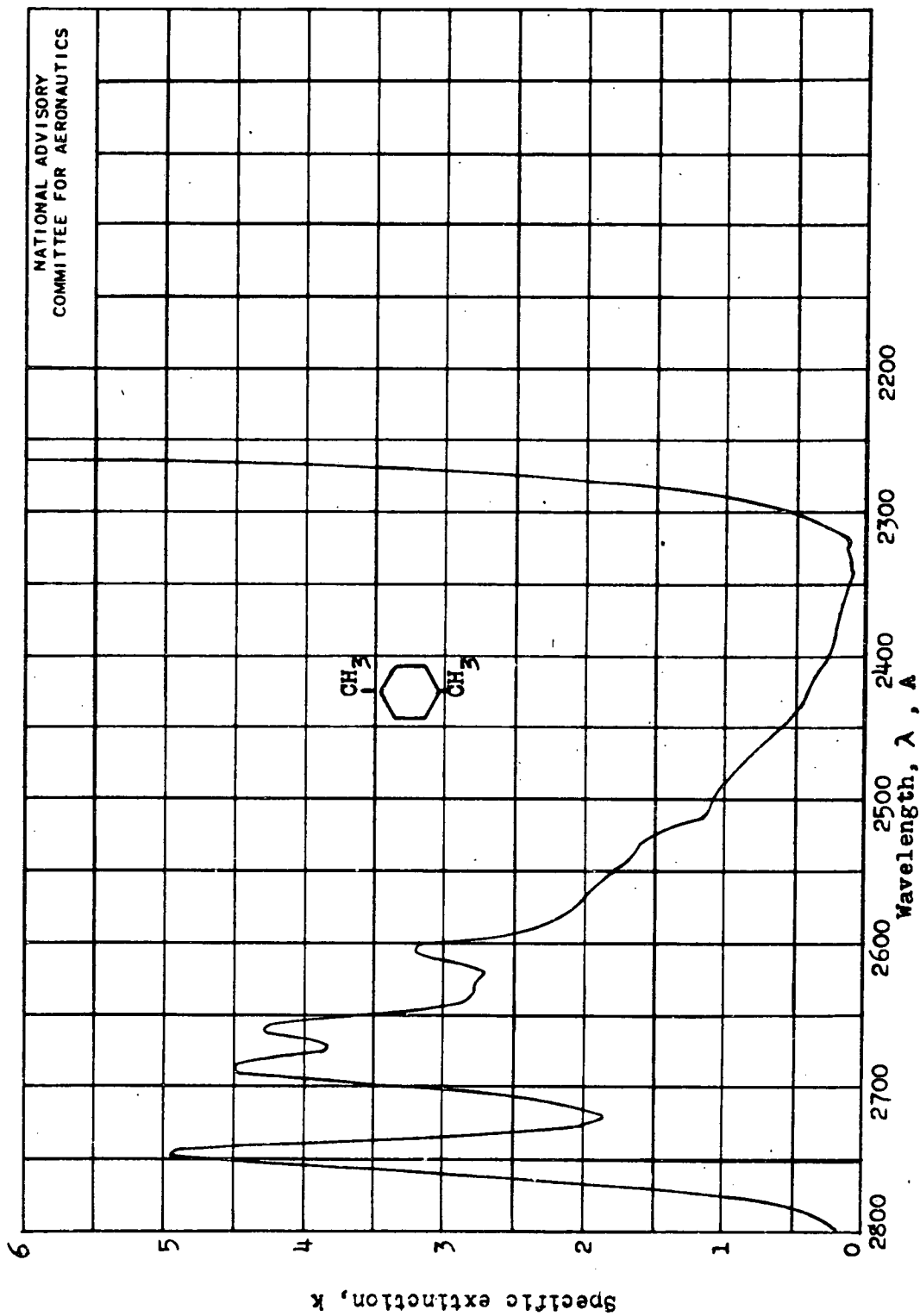


Figure 5. - Ultraviolet absorption spectrum of p-xylene determined by photoelectric spectrophotometer. Solvent, isooctane; slit widths, 0.50 millimeter.

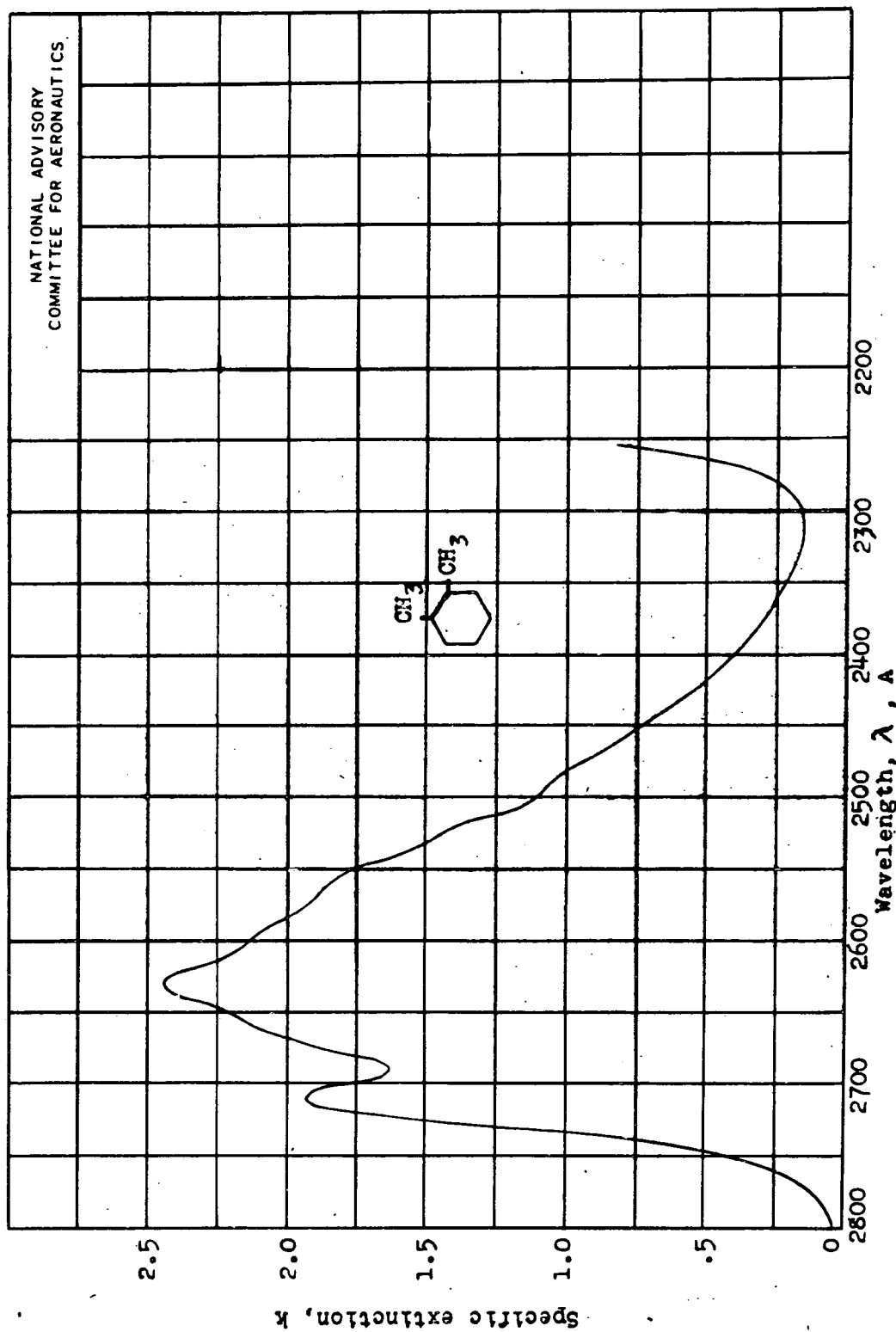


Figure 6. - Ultraviolet absorption spectrum of o-xylene determined by photoelectric spectrophotometer. Solvent, isooctane; slit widths, 0.50 millimeter.

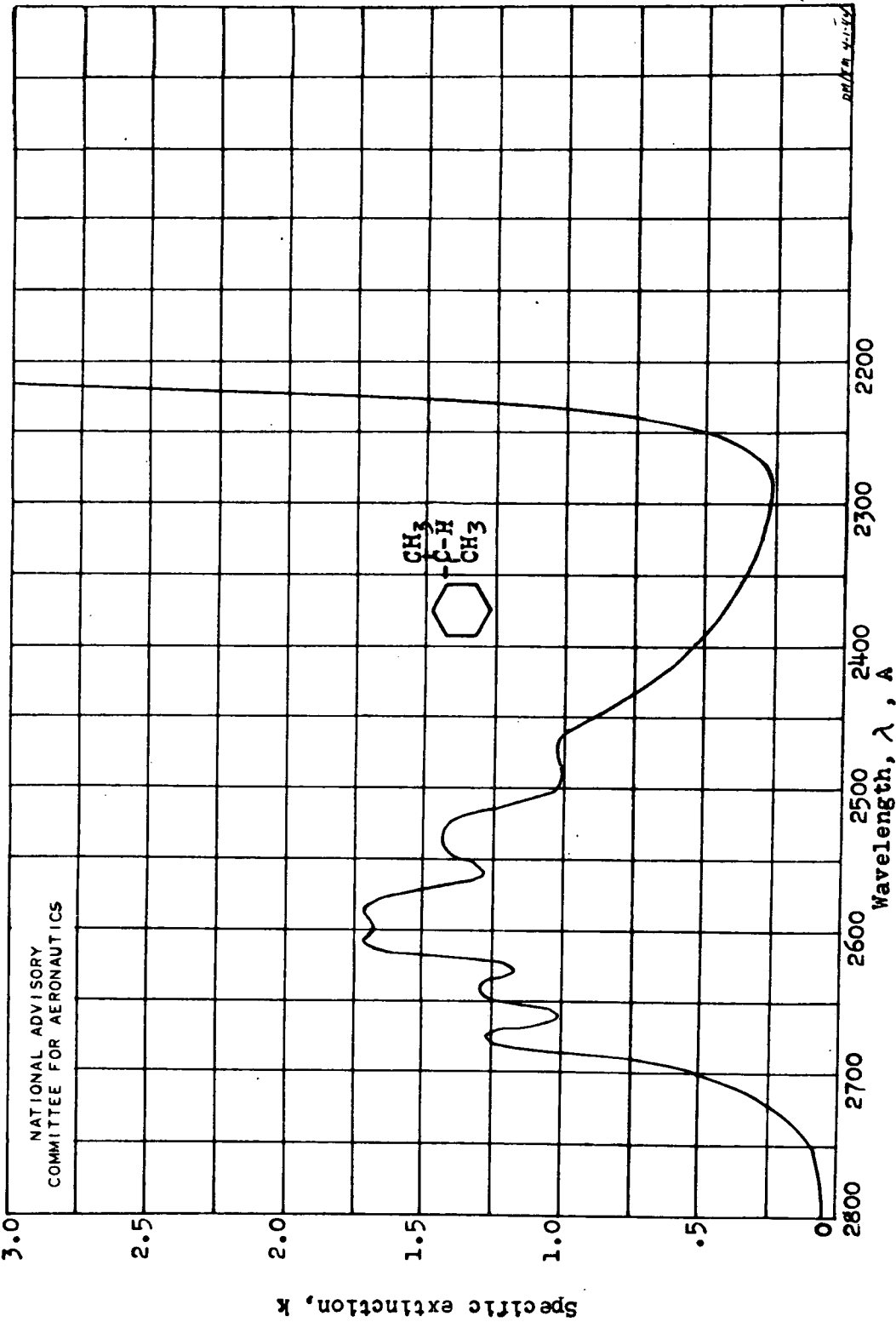


Figure 7. - Ultraviolet absorption spectrum of isopropylbenzene determined by photoelectric spectrophotometer. Solvent, isooctane; slit widths, 0.50 millimeter.

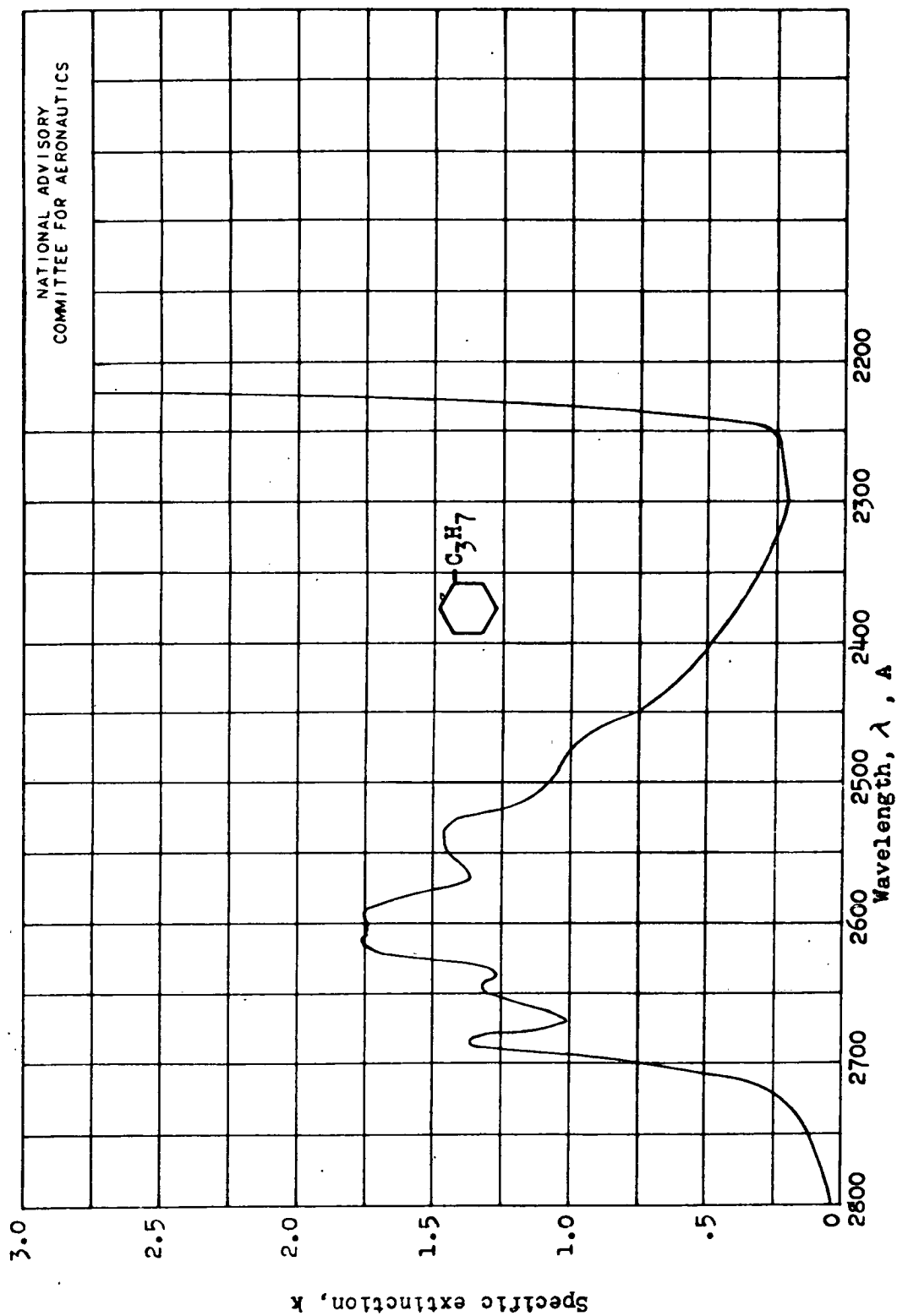


Figure 8. - Ultraviolet absorption spectrum of propylbenzene determined by photoelectric spectrophotometer. Solvent, isooctane; slit widths, 0.50 millimeter.

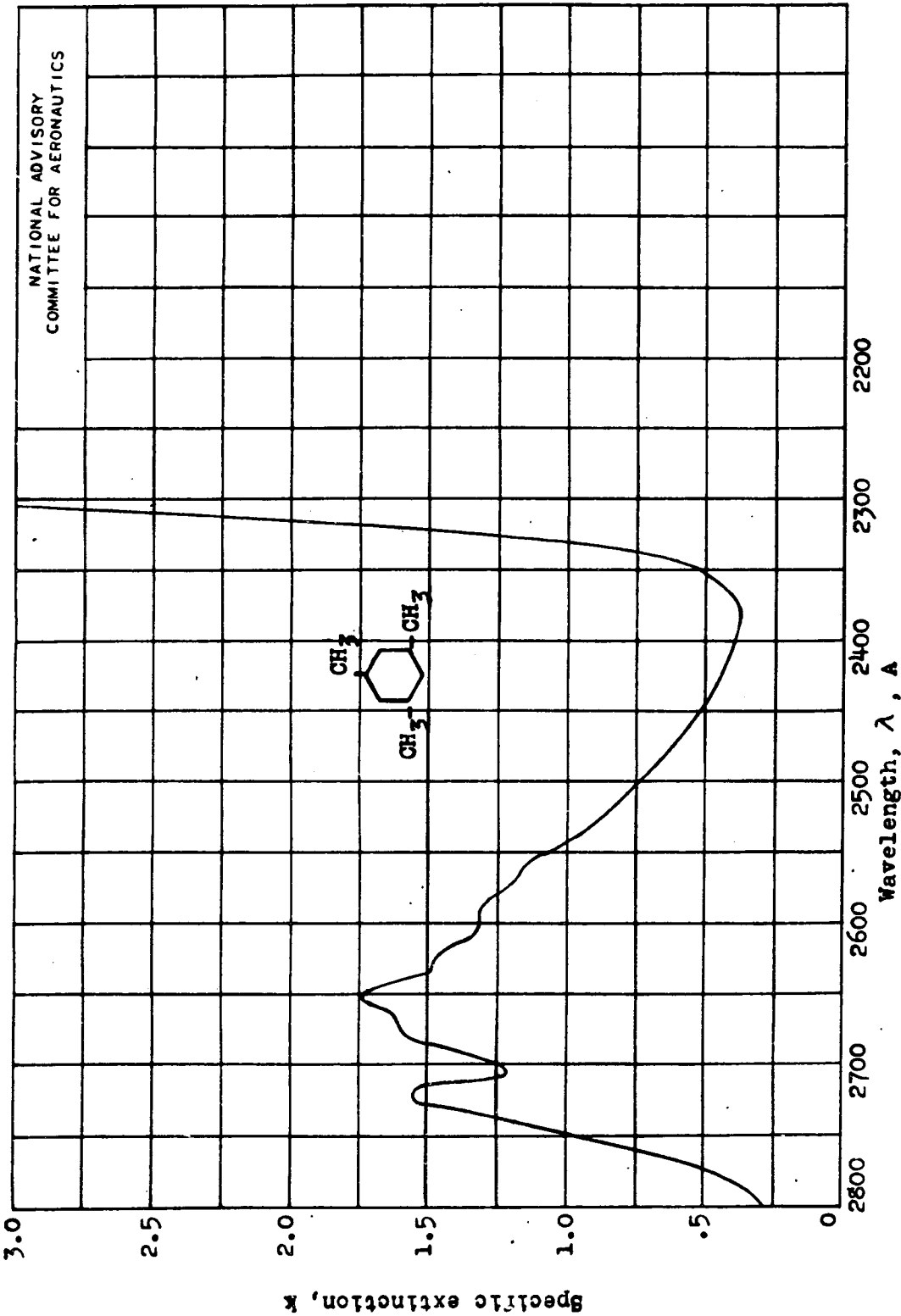


Figure 9. - Ultraviolet absorption spectrum of 1,3,5-trimethylbenzene determined by photoelectric spectrophotometer. Solvent, isooctane; slit widths, 0.50 millimeter.

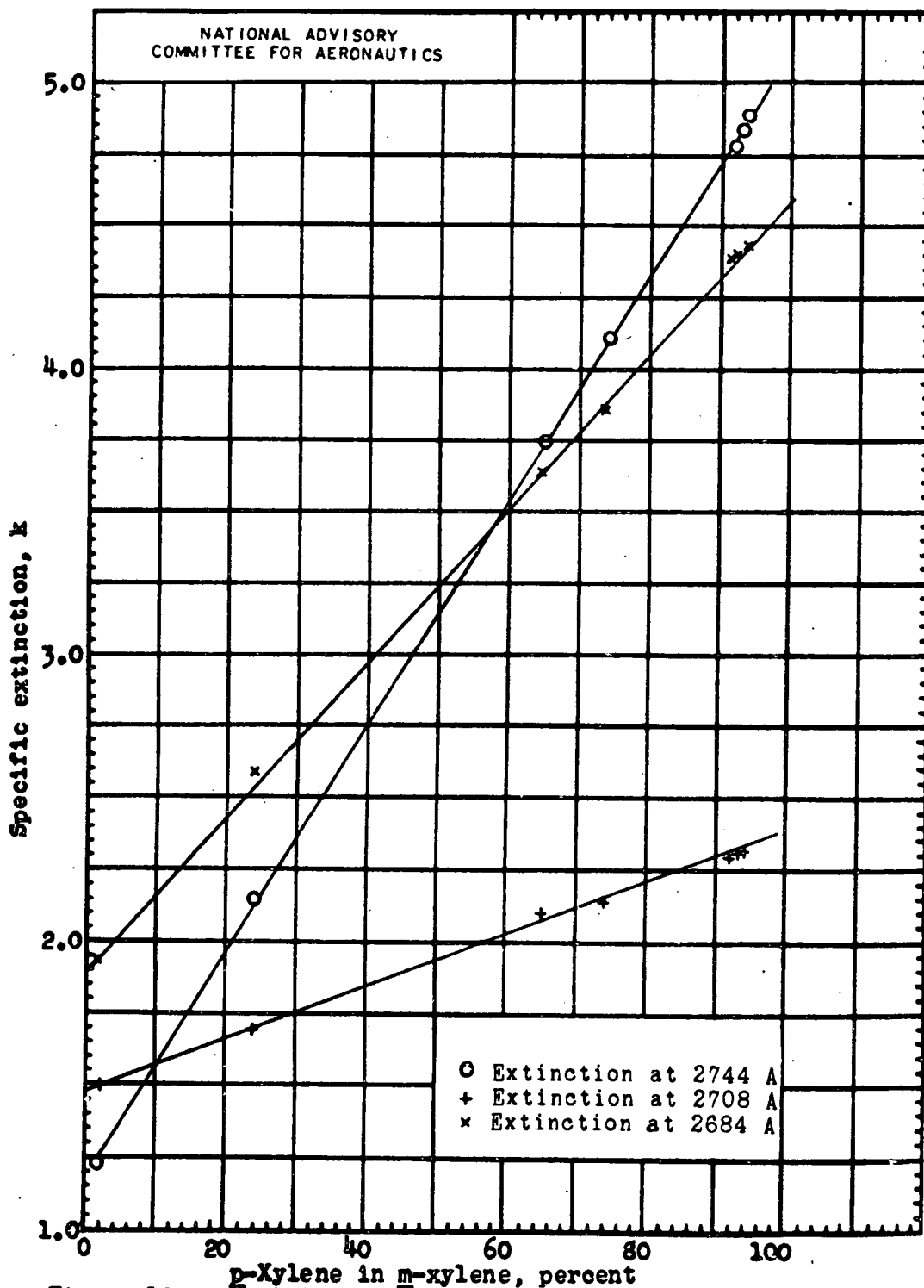


Figure 10. - Variation of specific extinction with percentage composition of a mixture of m-xylene and p-xylene. Solvent, isooctane; slit widths, 0.50 millimeter.